

HL - Organic Reactions

20.1-20.3

IB Chemistry

Topic 20

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Version 1.4

Topic 20.1

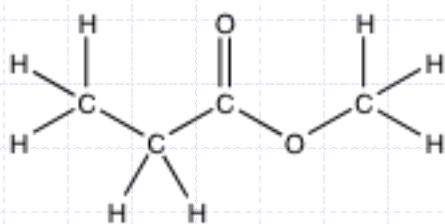
◆ 20.1 Introduction - 1 hour

- 20.1.1 Deduce structural formulas for compounds containing up to six carbon atoms with one of the following functional groups: amine, amide, ester and nitrile. (3)
- 20.1.2 Apply IUPAC rules for naming compounds containing up to six carbon atoms with one of the following functional groups: amine, amide, ester and nitrile. (2)

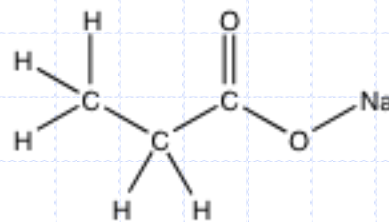


Ester Functional Group

◆ Esters are organic salts where the alkyl group of the alcohol has replaced the hydrogen of the carboxylic acid. Their name puts the alkyl group first followed by the name of the acid anion, for example:



methyl propionate
 $\text{C}_2\text{H}_5\text{COOCH}_3$



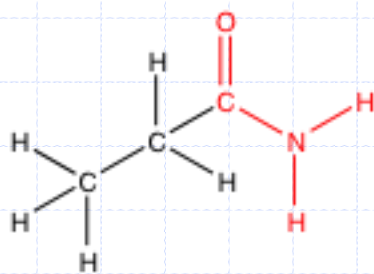
sodium propionate
 $\text{C}_2\text{H}_5\text{COONa}$



Amide Functional Group

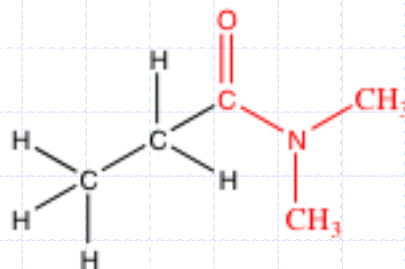
- Amides are acid derivatives where the -OH of the acid has been replaced by -NX_2 . Primary amides have an -NH_2 group; secondary and tertiary amides are substituted with respectively one and two alkyl groups bonded to the nitrogen. In these cases the substituent groups are named using N- and N,N- before the substituent.

Primary amide..



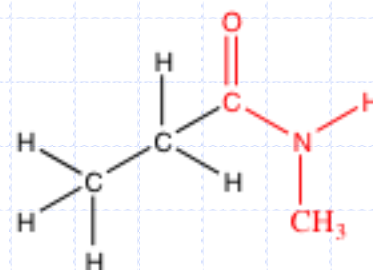
propionamide

Tertiary amide..



N,N-dimethylpropionamide

Secondary amide..



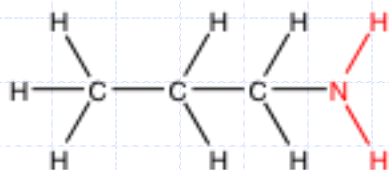
N-methylpropionamide



Amine Functional Group

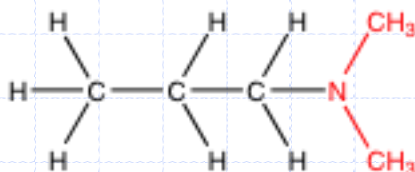
◆ Primary amines have an -NH_2 group which can undergo substitution by alkyl groups, giving rise to secondary and tertiary amines. These are named in a similar way to the amides, using N- to show the position of the substituents

Primary amine..



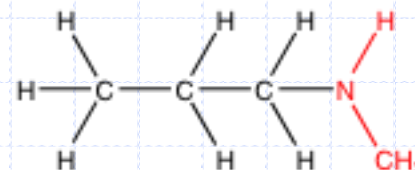
propan-1-amine

Tertiary amine..



N,N-dimethylpropan-1-amine

Secondary amine..



N-methylpropan-1-amine



Topic 20.2

◆ 20.2 Nucleophilic substitution reactions - 2 hours

- 20.2.1 Explain why the hydroxide ion is a better nucleophile than water. (3)
- 20.2.2 Describe and explain how the rate of nucleophilic substitution in halogenoalkanes by the hydroxide ion depends on the identity of the halogen. (3)
- 20.2.3 Describe and explain how the rate of nucleophilic substitution in halogenoalkanes by the hydroxide ion depends on whether the halogenoalkane is primary, secondary or tertiary. (3)
- 20.2.4 Describe, using equations, the substitution reactions of halogenoalkanes with ammonia and potassium cyanide. (2)
- 20.2.5 Explain the reactions of primary halogenoalkanes with ammonia and potassium cyanide in terms of the S_N2 mechanism. (3)
- 20.2.6 Describe, using equations, the reduction of nitriles using hydrogen and a nickel catalyst. (2)



20.5 - Reaction Pathways and mechanisms

- ◆ Most organic reactions proceed by a defined sequence or set of steps. The detailed **pathway** which an organic reaction follows is called a **mechanism**.
- ◆ Knowing a reaction mechanism is very valuable information. It allows the chemist to predict what products will be formed when a chemical reaction occurs.
- ◆ The organic chemist can use this information to modify compounds and to synthesize new compounds with certain desired characteristics.



Diagram of common organic reactions

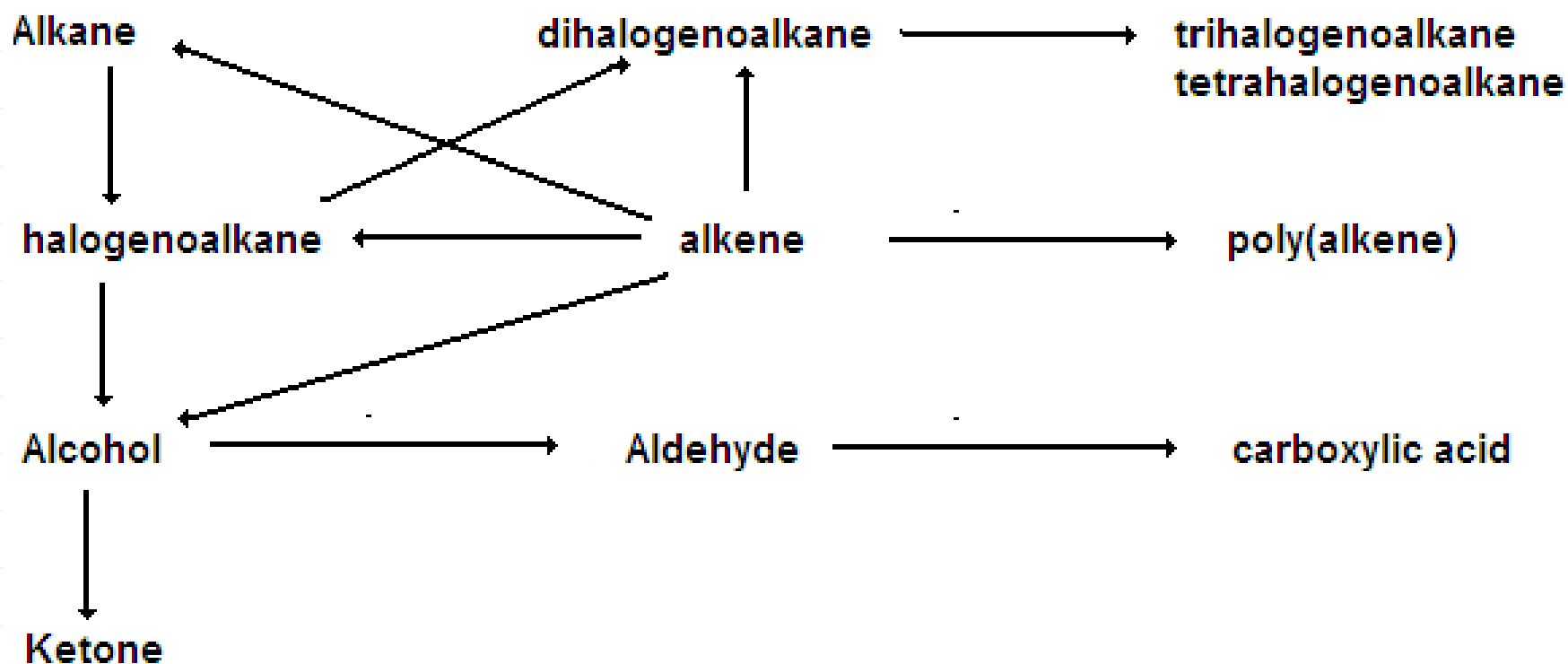
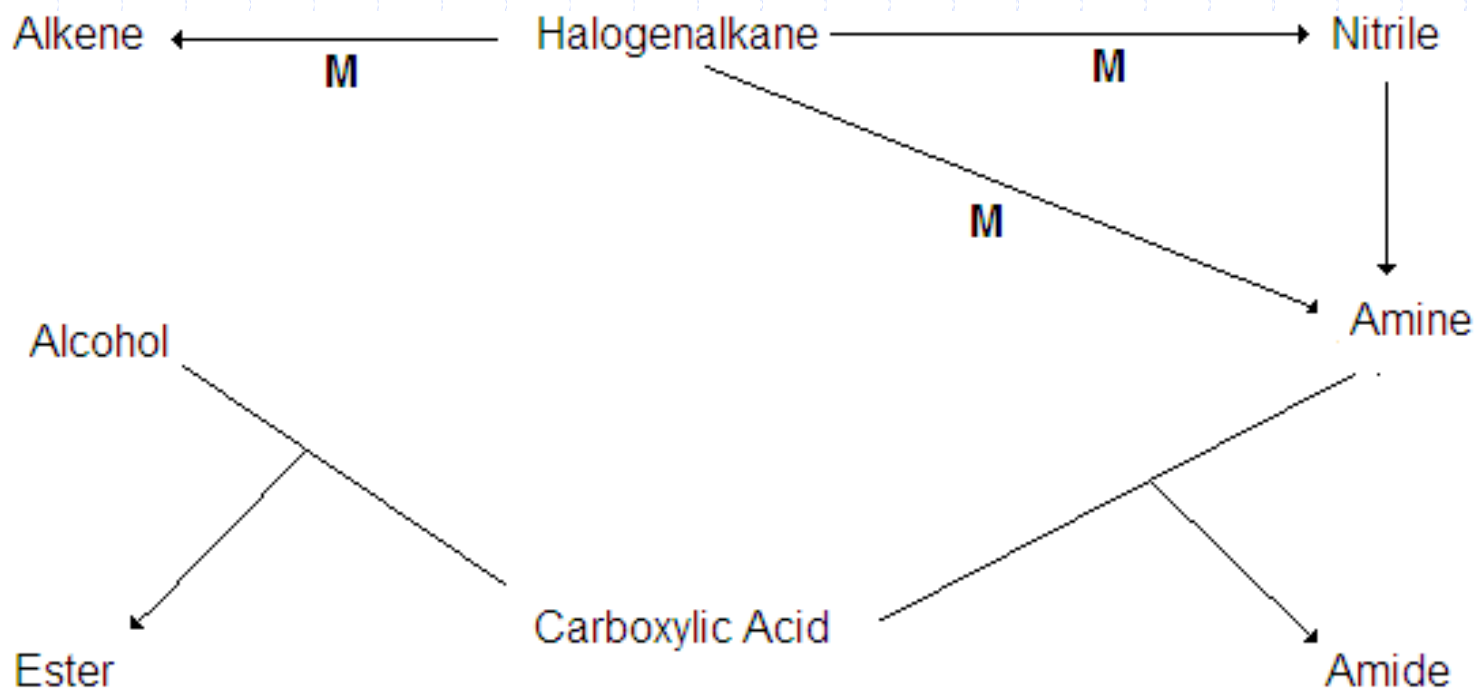


Diagram of common organic reactions



M = mechanism required



Substitution Reactions

◆ In a **substitution** reaction, one atom or group of atoms, takes the place of another in a molecule

◆ Examples



Nucleophilic Substitution

- ◆ A **nucleophile** is a molecule or ion that has a high electron density.
- ◆ It is attracted to atoms in molecules with a lower electron density.
- ◆ It may replace another group in an organic molecule.
- ◆ The molecule to which the nucleophile is attracted is called the **substrate**
- ◆ The group that the nucleophile replaces is called the **leaving group**
- ◆ These reactions are known as **nucleophilic** substitutions.



Nucleophilic Substitution

- ◆ One covalent bond is broken as a new covalent bond is formed
- ◆ The general form for the reaction is

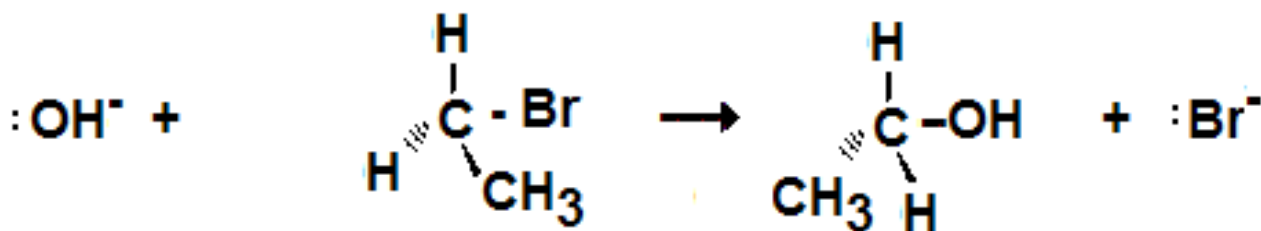


Nucleophile

Substrate

Product

Leaving group



Nucleophilic Substitution

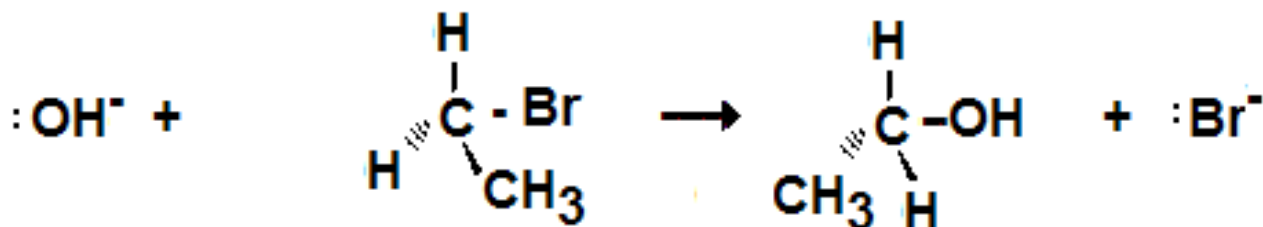
- ◆ $\text{Nu:}^- + \text{R-X} \rightarrow \text{R-Nu} + \text{X:}$
- ◆ The bond to the leaving group is broken
- ◆ The leaving group takes both electrons that formed the bond with it
- ◆ The nucleophile provides the electrons to form the new bond

Nucleophile

Substrate

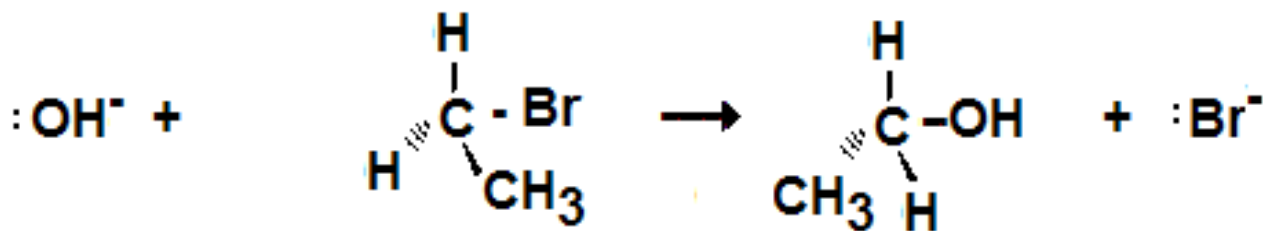
Product

Leaving group



Nucleophilic Substitution

- ◆ Alkyl halides commonly undergo nucleophilic substitution reactions. The nucleophile displaces the halide leaving group from the alkyl halide.
- ◆ There are two common ways for nucleophilic substitutions to occur. They are known as S_N1 and S_N2 .



Nucleophile

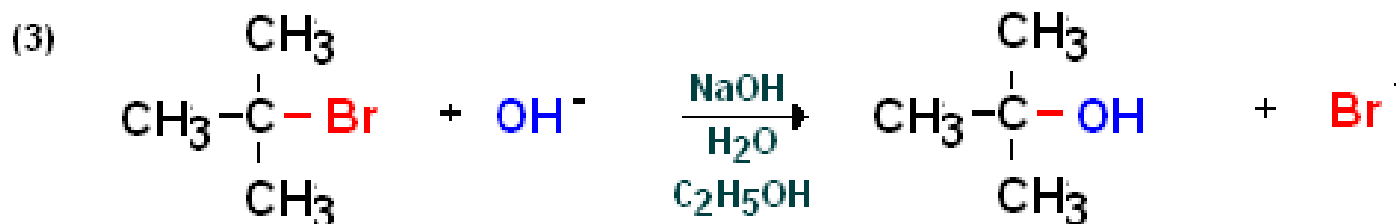
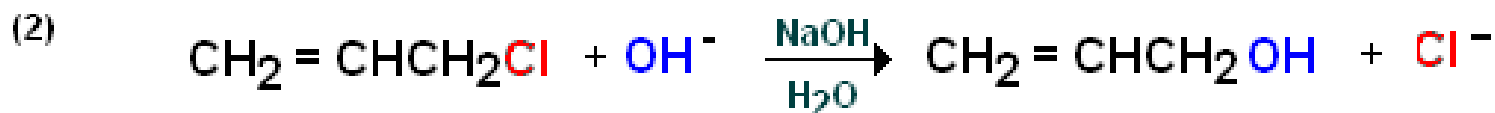
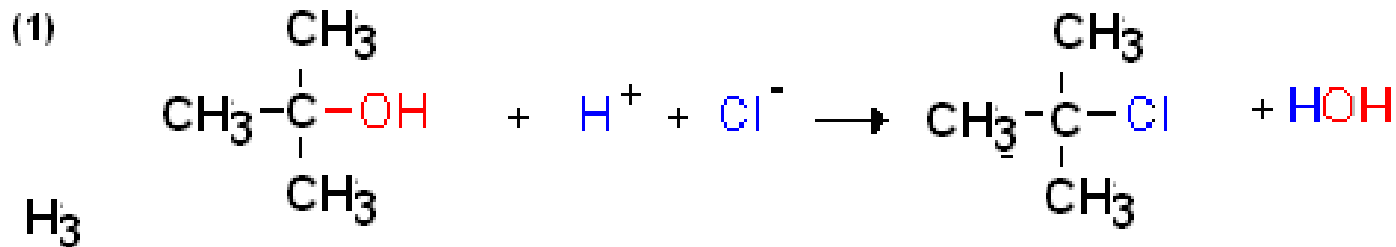
Substrate

Product

Leaving group



Examples of Nucleophilic Substitutions



◆ **Nucleophilic** substitutions may be S_N1 or S_N2

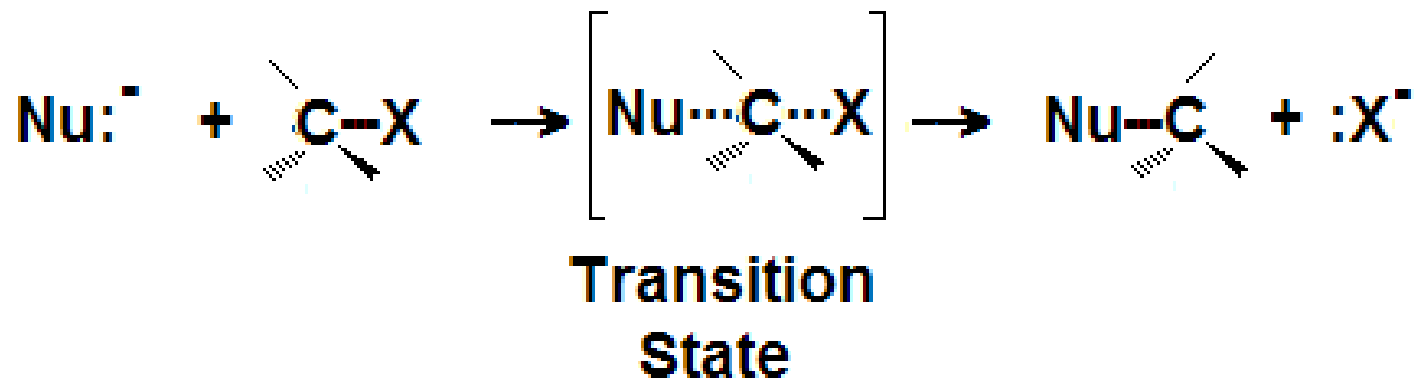
Nucleophilic Substitution

Bimolecular or S_N2

- ◆ A reaction is **bimolecular** when the rate depends on both the concentration of the **substrate** and the **nucleophile**.
- ◆ S_N2 mechanisms occur most readily with methyl compounds and **primary** haloalkanes



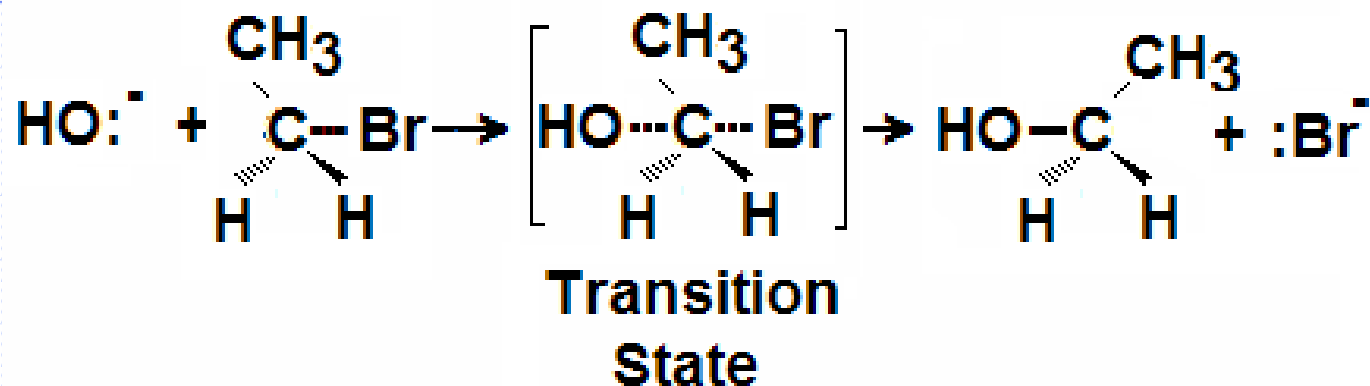
S_N2 Mechanism



The general form for an S_N2 mechanism is shown above.
Nu:- = nucleophile



An Example of a S_N2 Mechanism



The nucleophilic substitution of ethyl bromide is shown above. This reaction occurs as a bimolecular reaction. The rate of the reaction depends on both the concentration of both the hydroxide ion and ethyl bromide

- ◆ This is a **one step process** since both the nucleophile and the substrate must be in a rate determining step.



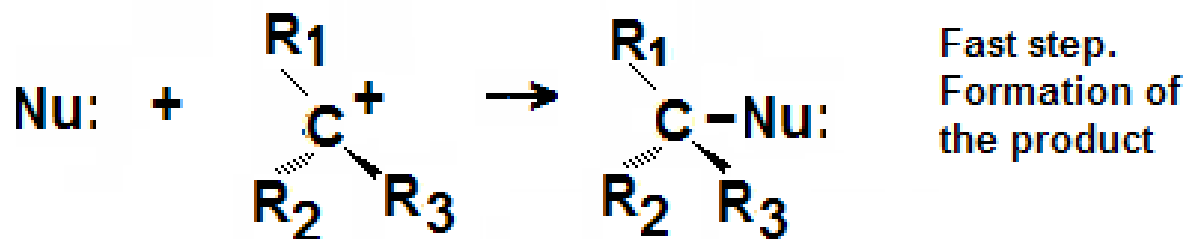
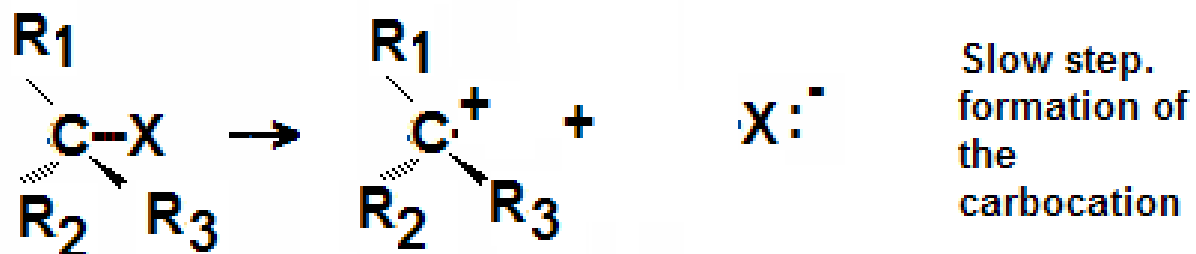
Nucleophilic Substitution

Unimolecular or S_N1

- ◆ A unimolecular reaction occurs when the rate of reaction depends on the concentration of the substrate but not the nucleophile.
- ◆ A unimolecular reaction is a two step process since the substrate and the nucleophile cannot both appear in the rate determining step
- ◆ S_N1 mechanisms occur most readily with **tertiary** haloalkanes and some secondary haloalkanes.



S_N1 Mechanism

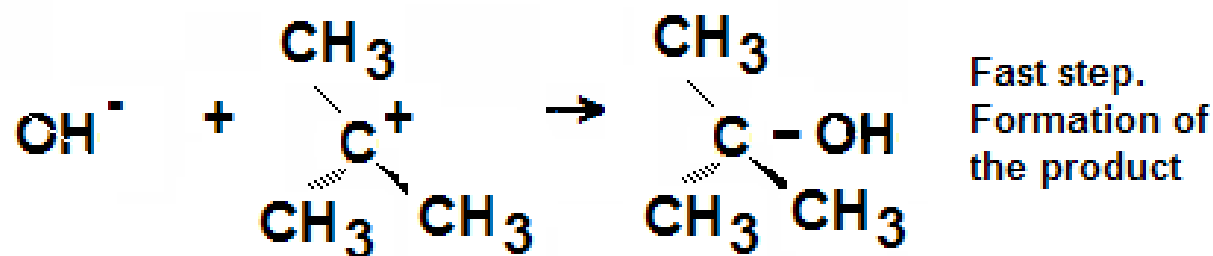
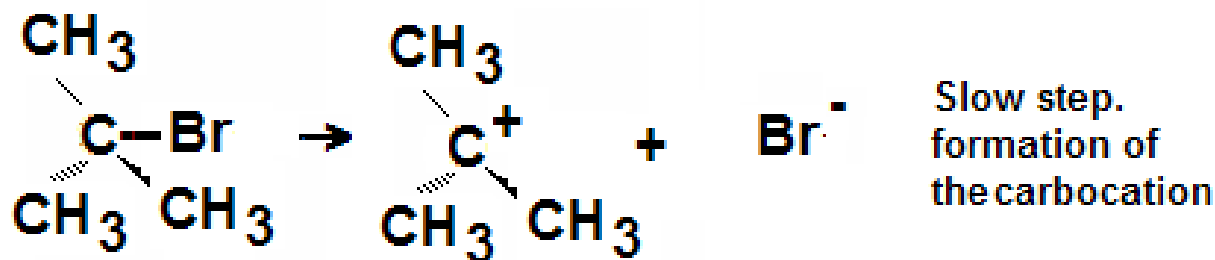


The general form for an S_N1 mechanism is shown above.

Nu:- = nucleophile



S_N1 Mechanism



The first step is the formation of the **carbocation**. It is the slow step. The rate of the reaction depends only on the concentration of the substrate.



S_N1 and S_N2 Reactions

	S_N1	S_N2
Rate	$=k[RX]$	$=k[RX][Nuc:]^-]$
Carbocation intermediate?	Yes	No
Stereochemistry	mix	Inversion of configuration
Rearrangement	$\sim H, \sim CH_3$ possible	No rearrangements



Topic 10.2.3 Review

- ◆ Reactions of alkanes with halogens
- ◆ Requires radicals



Free Radical Substitutions

- ◆ Many organic molecules undergo substitution reactions.
- ◆ In a substitution reaction one atom or group of atoms is removed from a molecule and replaced with a different atom or group.
- ◆ Example:



Three Basic Steps in a Free Radical Mechanism

◆ *Chain initiation*

The chain is initiated (started) by UV light breaking a chlorine molecule into free radicals.



◆ *Chain propagation reactions*

These are the reactions which keep the chain going.



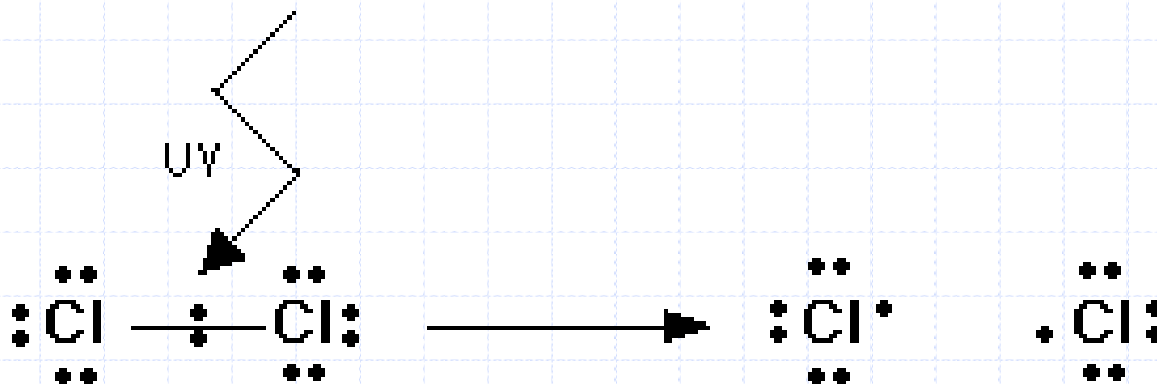
◆ *Chain termination reactions*

These are reactions which remove free radicals from the system without replacing them by new ones.



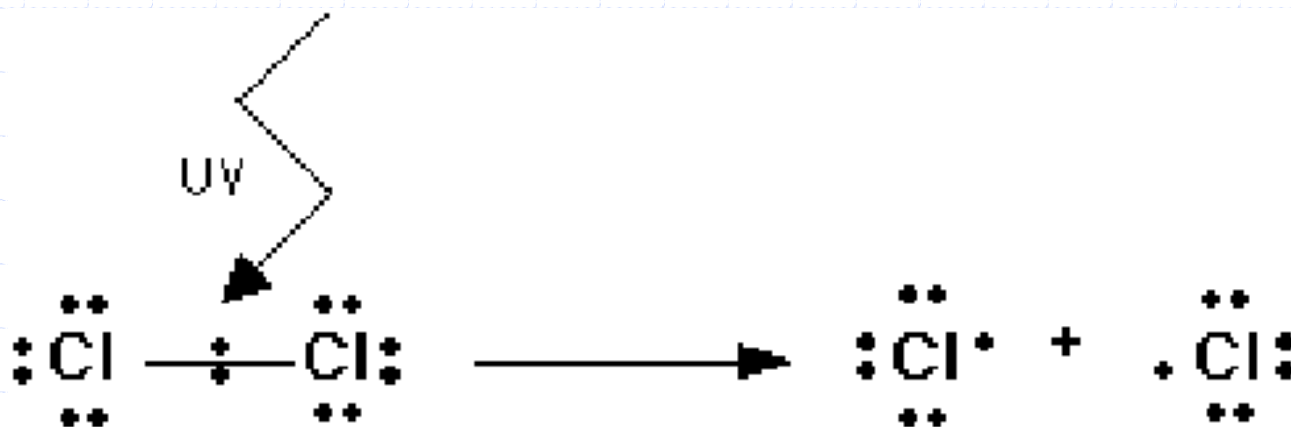
Free Radical Mechanism-The Initiation Step

- ◆ The ultraviolet light is a source of energy that causes the chlorine molecule to break apart into 2 chlorine atoms, each of which has an unpaired electron
- ◆ The energies in UV are exactly right to break the bonds in chlorine molecules to produce chlorine atoms.



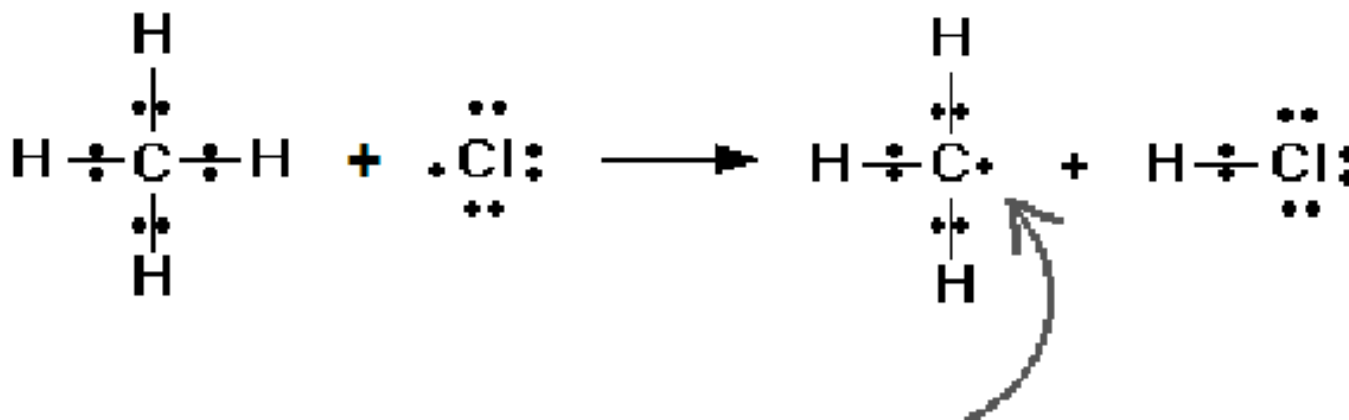
Homolytic Fission

- ◆ Free radicals are formed if a bond splits evenly - each atom getting one of the two electrons. The name given to this is ***homolytic fission***.



Free Radical Propagation

- ◆ The **productive collision** happens if a chlorine radical hits a methane molecule.
- ◆ The chlorine radical removes a hydrogen atom from the methane. That hydrogen atom only needs to bring one electron with it to form a new bond to the chlorine, and so one electron is left behind on the carbon atom. A new free radical is formed - this time a methyl radical, CH_3 .



A new free radical is formed



Free Radical Propagation II

- ◆ If a methyl radical collides with a chlorine molecule the following occurs:



- ◆ The methyl radical takes one of the chlorine atoms to form chloromethane
- ◆ In the process generates another chlorine free radical.
- ◆ This new chlorine radical can now go through the whole sequence again, It will produce yet another chlorine radical - and so on and so on.



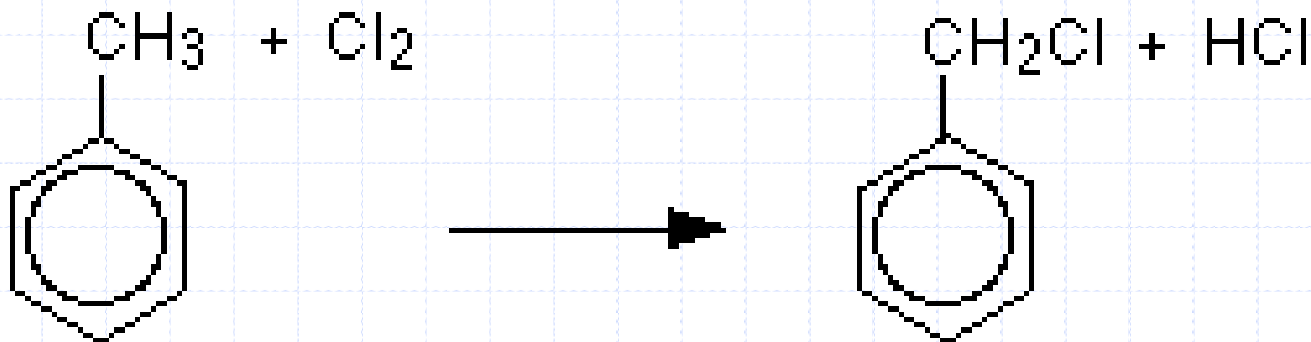
Termination Steps

- ◆ The free radical propagation does not go on for ever.
- ◆ If two free radicals collide the reaction is terminated.



Exercise

- ◆ Write the steps in the free radical mechanism for the reaction of chlorine with methyl benzene. The overall reaction is shown below. The methyl group is the part of methyl benzene that undergoes attack.

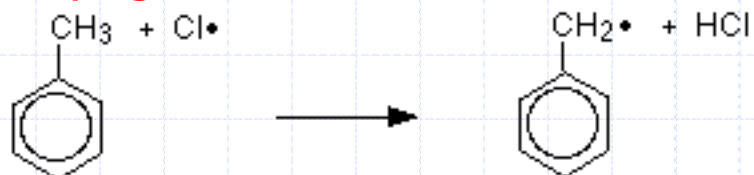


Solution

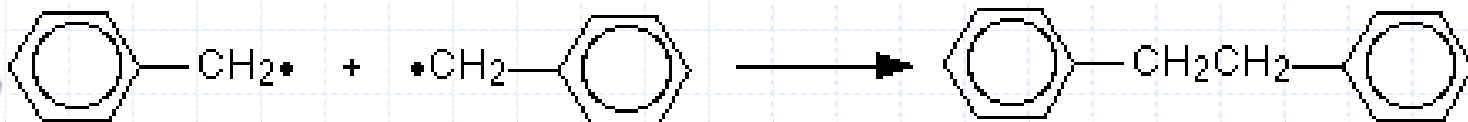
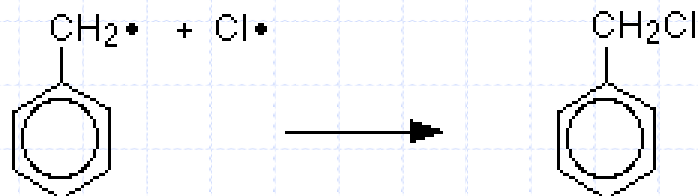
◆ Initiation



◆ Propagation



■ Termination



Electrophilic Addition



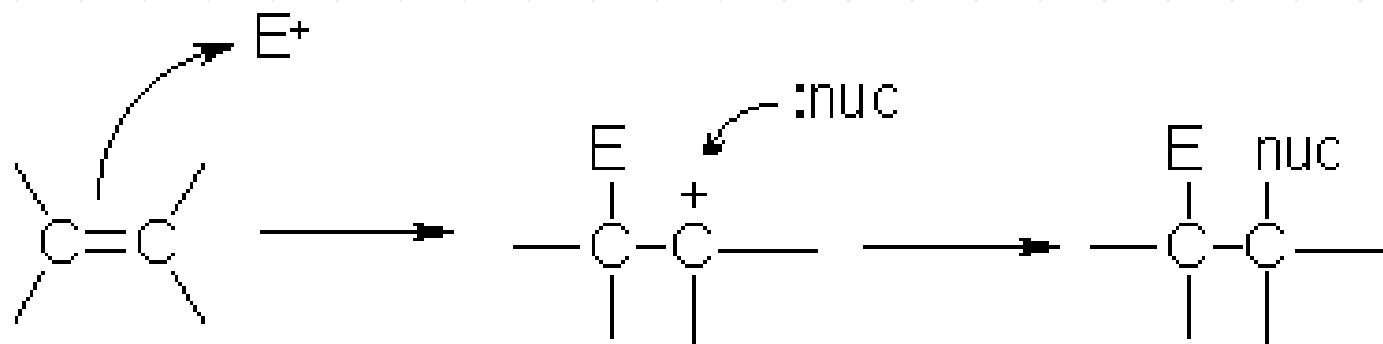
Addition Mechanisms

- ◆ **Electrophilic addition** occurs in reactions involving containing carbon-carbon double bonds - the alkenes.
- ◆ An **electrophile** is a molecule or ion that is attracted to electron-rich regions in other molecules or ions.
- ◆ Because it is attracted to a negative region, an electrophile carries either a positive charge or a partial positive charge



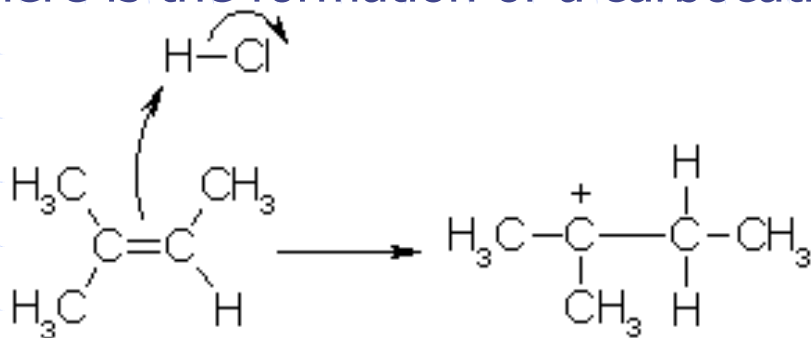
Electrophilic Addition II

Electrophilic addition occurs in molecules where there are delocalized electrons. The electrophilic addition to alkenes takes the following general form:

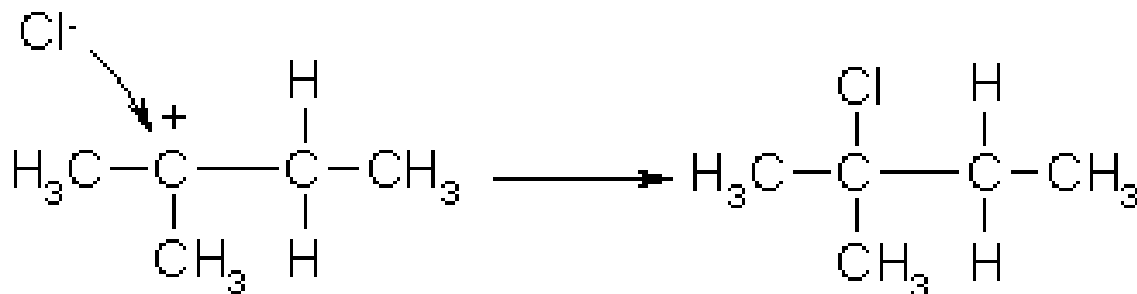


Electrophilic Addition II

The electrophilic addition of alkanes occurs in two stages
First there is the formation of a carbocation

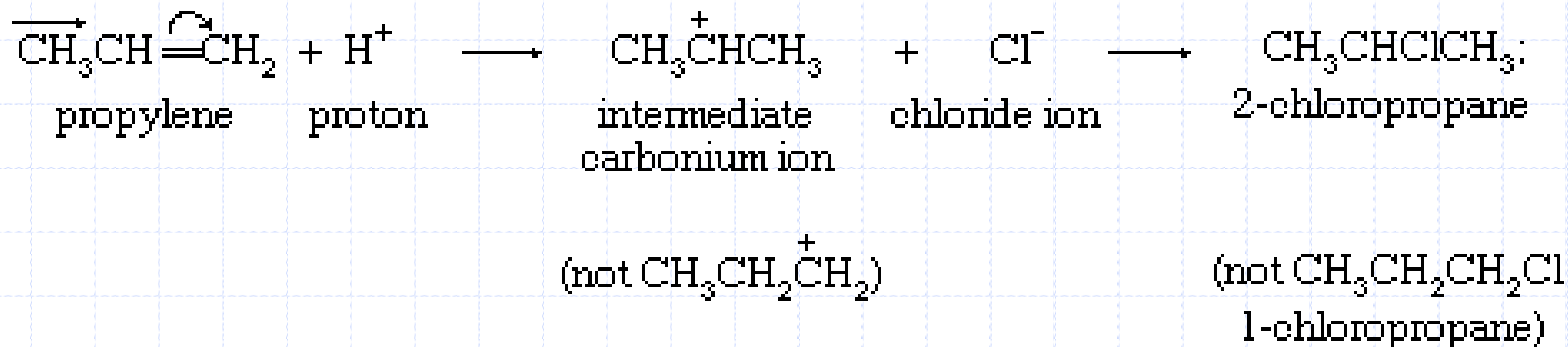


Followed by the attack the chloride ion to form the addition product



Markovnikoff's Rule

Actually there are two possible carbocations that could be formed. In many cases this would result in two possible products. However only one form is preferred



"Birds of a feather flock together!"

The hydrogen ion will tend to migrate to the side with the greater number of hydrogen atoms. This preference is known as Markovnikoffs Rule.



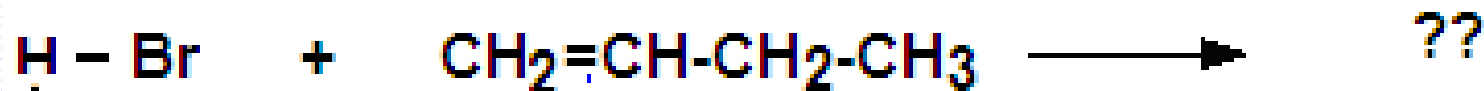
Electrophilic Additions

- ◆ An addition reaction is a reaction in which two molecules join together to make a larger molecule. There is only one product. All the atoms in the original molecules are found in the single product molecule.
- ◆ An electrophilic addition reaction is an addition reaction which happens because what we think of as the "important" molecule is attacked by an electrophile. The "important" molecule has a region of high electron density which is attacked by something carrying some degree of positive charge.



Exercise

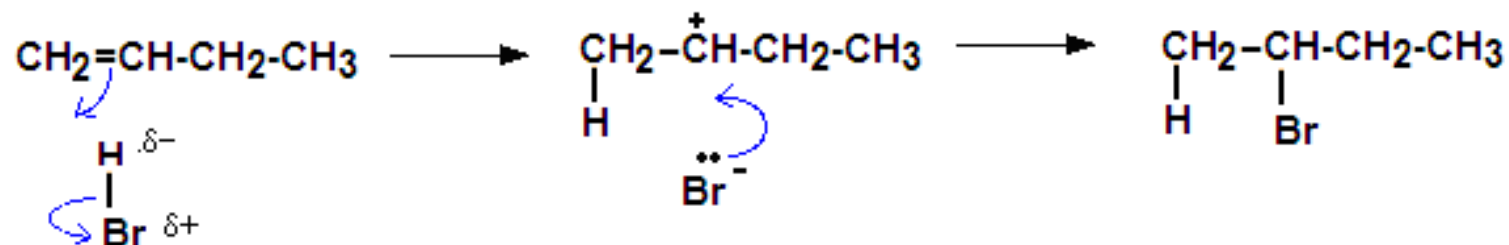
Write a mechanism for the electrophilic addition of HBr to 1-butene.



Solution

Write a mechanism for the electrophilic addition of HBr to 1-butene.

Solution



Topic 20.3

◆ 20.3 Elimination reactions - 1 hour

- 20.3.1 Describe, using equations, the elimination of HBr from bromoalkanes. (2)
- 20.3.2 Describe and explain the mechanism for the elimination of HBr from bromoalkanes. (3)



Elimination Reactions

- ◆ An **elimination reaction** is a type of organic reaction in which two substituents are removed from a molecule in either a one or two-step mechanism
- ◆ In most organic elimination reactions the unsaturation level of the molecule increases.



Elimination Reactions

 Elimination reactions may be either:

----- **Unimolecular** (Designated **E1**)

Two steps. The reaction rate depends on the concentration of the substrate

----- **Bimolecular** (Designated **E2**)

One step. The reaction rate depends on the concentration of both the substrate and the other reacting species



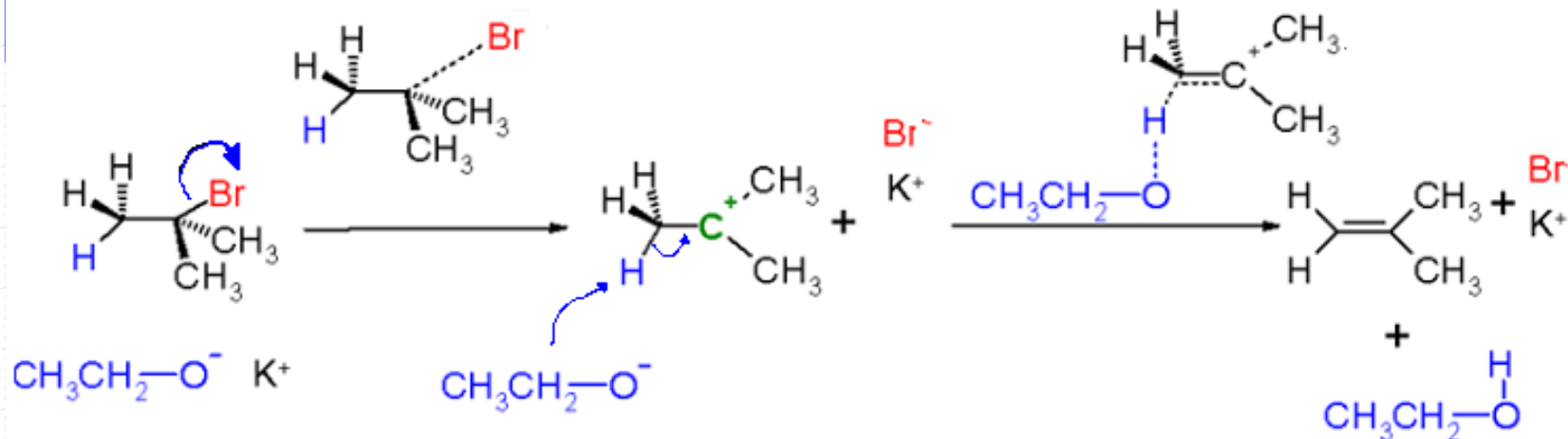
E1—Unimolecular Elimination

- ◆ Occurs in two steps
- ◆ Reaction rate depends primarily on the concentration of the substrate



E1 Unimolecular elimination

- ◆ Occurs in two steps: First there is the formation of the intermediate and then the formation of the C=C.
- ◆ Occurs in tertiary and secondary haloalkanes.



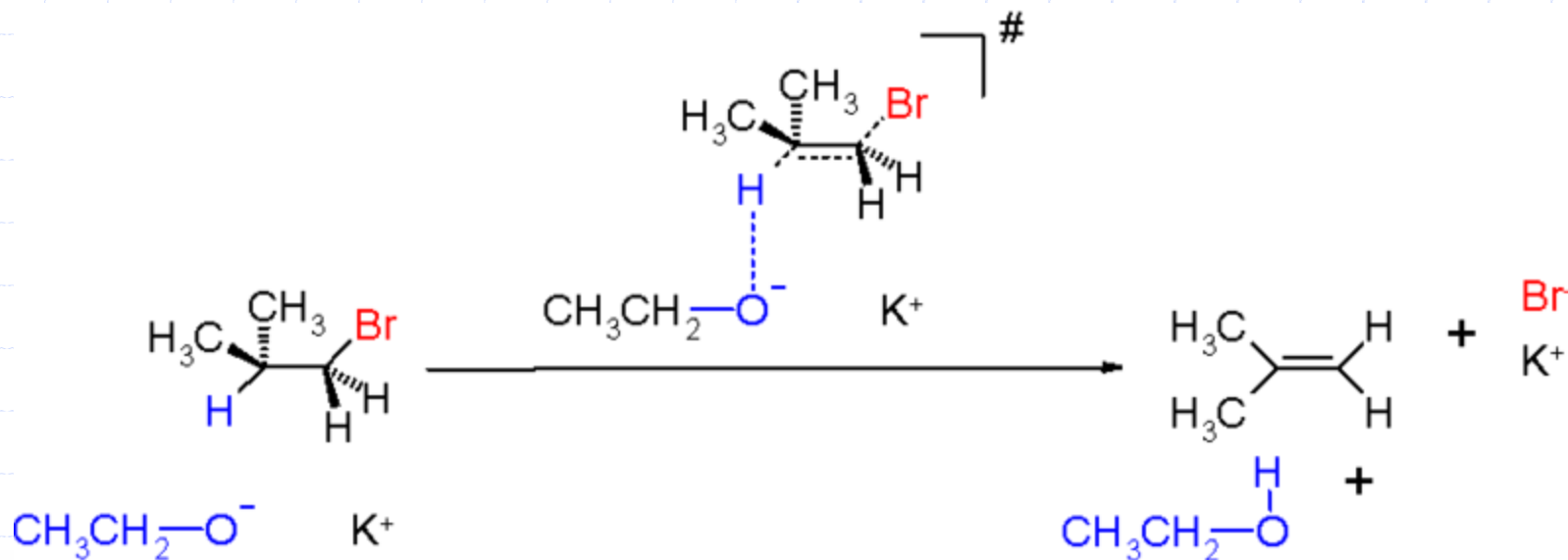
E2 Bimolecular Elimination

- ◆ Reaction occurs in essentially one rate determining step
- ◆ Reaction rate depends on the concentration of both reactants



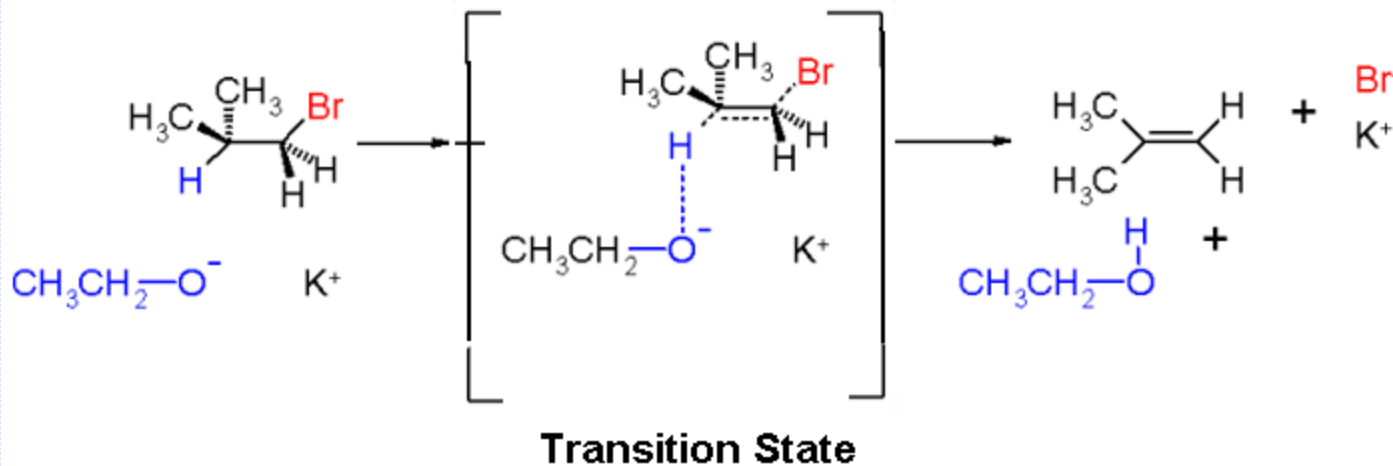
Example of E2

- ◆ A strong base is used to remove a hydrogen atom and a bromine atom from the haloalkane to form the unsaturated alkene.
- ◆ Occurs in primary haloalkanes



Example of E2

- ◆ A strong base is used to remove a hydrogen atom and a bromine atom from the haloalkane to form the unsaturated alkene.
- ◆ Occurs in primary haloalkanes



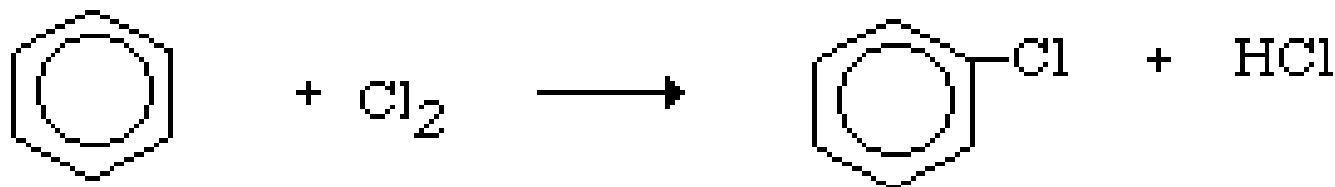
Electrophilic Substitution

- ◆ The displacement reactions of the alkyl halides do not usually work for aromatic (aryl) halides unless a halogen is part of a side chain.
- ◆ A halogen atom held to a double bonded carbon atom is usually rather unreactive, Likewise a halogen atom attached to a benzene ring is very stable and unlikely to react.
- ◆ Most aromatic substitution reactions proceed by a mechanism known as **electrophilic** substitution



Electrophilic Substitution

- ◆ An example of an electrophilic substitution is the reaction of chlorine with a benzene ring.
- ◆ The overall reaction is



The mechanism for this reaction involves 3 steps



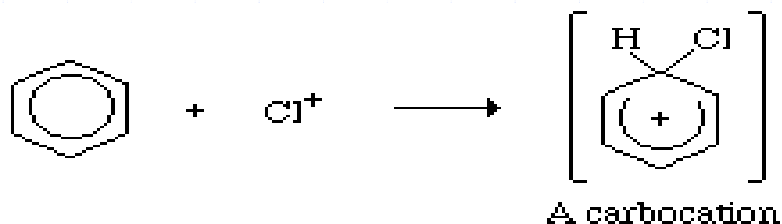
Electrophilic Substitution

-3 Steps

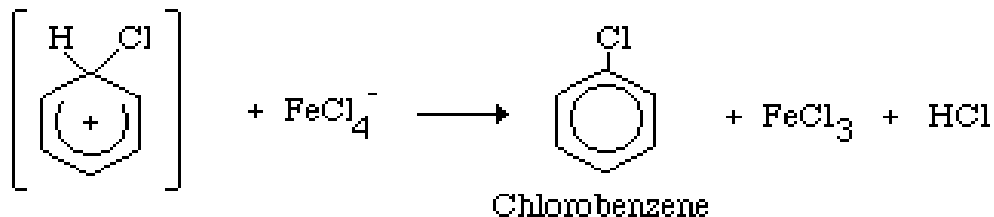
- ◆ The initial step is the formation of the **electrophile**. A catalyst may be required.



- ◆ The second step is the attachment of the electrophile to the benzene ring forming the carbocation.



- The final step is the loss of hydrogen to form the product.



Electrophilic Substitutions

- ◆ The delocalized electrons found in the benzene ring are a source of electrons for electrophilic substitutions.
- ◆ The reactivity of the benzene ring is related to the kind of substituents attached to the ring.
- ◆ For example:

Methyl benzene reacts much more rapidly with sulfuric acid than benzene. The presence of the methyl group attached to the ring changes the overall electron density of the ring.

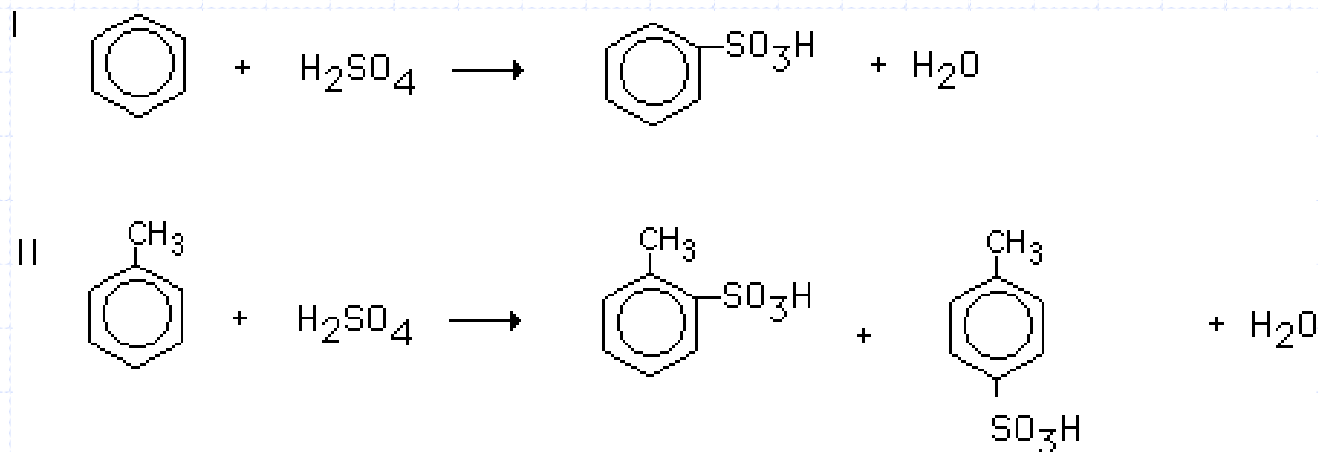
The methyl group in essence increases the electron density of the ring.
- ◆ Substances that increase the overall electron density of the ring are called activators



Ring Substitution

- ◆ The type of substituent on the ring influences where the substitution will occur.

- ◆ Case 1

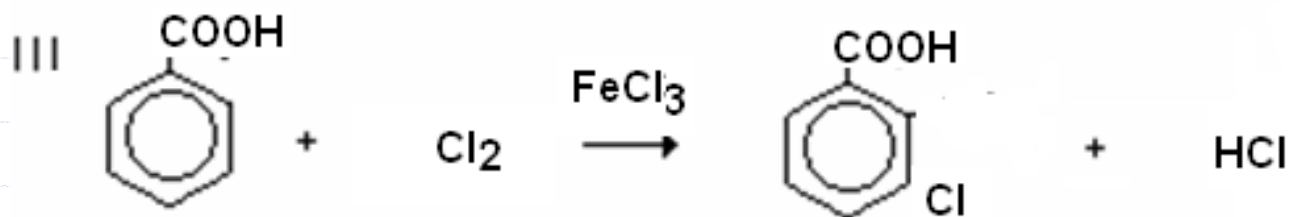


- The presence of the methyl group results in the attachment of the sulfonate group at the second and fourth carbons. It is known as an ortho/para director.



Ring Substitution

◆ Case 2



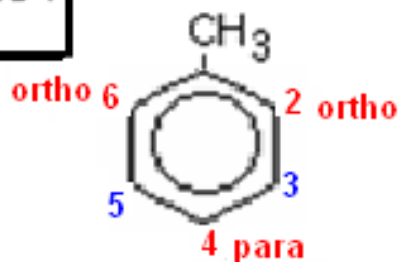
- The presence of the presence of a carboxyl group on the ring causes the chlorine to attach at the third position. It is called a **meta director**



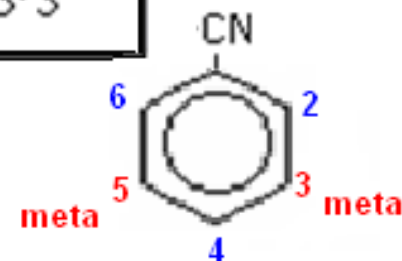
Ring Substitution

- ◆ Certain groups to the benzene ring cause new groups to attach at carbons 2 and 4. They are called **ortho/para directors**. Other groups cause the new group to attach at carbons 3 and 5. They are known as **meta directors**.

Ortho/para directors
$-\text{CH}_3$
$-\text{OH}$
$-\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$
F, Cl, Br, and I



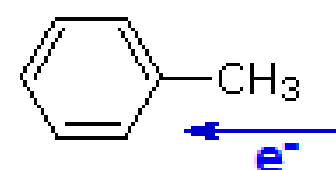
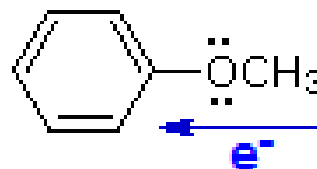
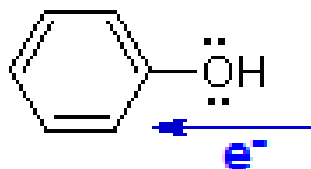
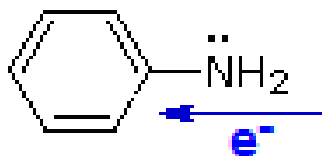
Meta directors
$-\text{NO}_2$
$-\text{CN}$
$-\text{COOH}$
$-\text{SO}_3\text{H}$
$-\text{CHO}$
$-\text{N}-(\text{CH}_3)_3^+$



Ring Activation

- ◆ When certain groups are attached to a benzene ring they tend to push electrons to the ring.
- ◆ The substituted benzene ring is more reactive than benzene itself
- ◆ These groups are known as ring activators

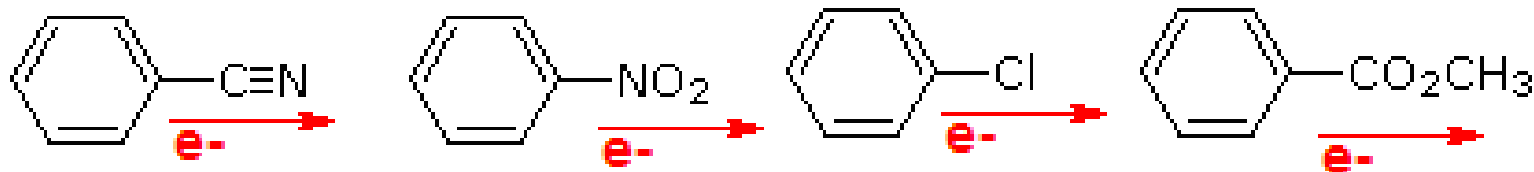
Activating Substituents



Ring Deactivation

- ◆ When certain groups are attached to a benzene ring they tend to pull electrons from the ring.
- ◆ The substituted benzene ring is less reactive than benzene itself
- ◆ These groups are known as ring deactivators

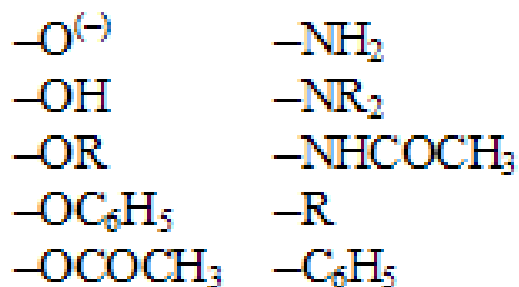
Deactivating Substituents



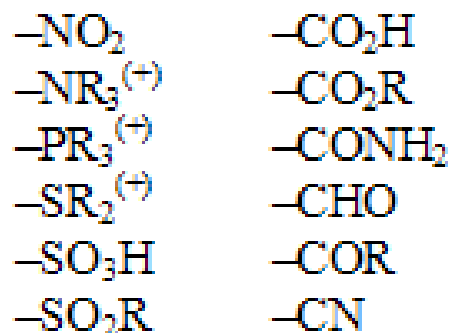
Electrophilic Substitution

◆ Summary

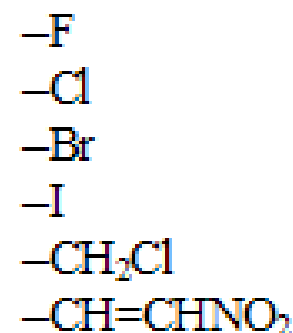
Activating Substituents ortho & para- Orientation



Deactivating Substituents meta-Orientation



Deactivating Substituents ortho & para- Orientation



Exercises

- ◆ Propose a mechanism and determine the products for the reaction of



Topic 20.4

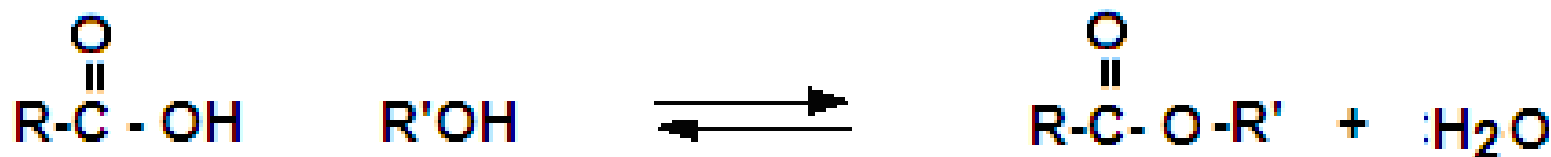
◆ 20.4 Condensation reactions - 2 hours

- 20.4.1 Describe, using equations, the reactions of alcohols with carboxylic acids to form esters, and state the uses of esters. (2)
- 20.4.2 Describe, using equations, the reactions of amines with carboxylic acids. (2)
- 20.4.3 Deduce the structures of the polymers formed in the reactions of alcohols with carboxylic acids. (3)
- 20.4.4 Deduce the structures of the polymers formed in the reactions of amines with carboxylic acids. (3)
- 20.4.5 Outline the economic importance of condensation reactions. (2)



Condensation Reactions

◆ The condensation of an acid and an alcohol results in the formation of an ester and water.



The carbon chain from the alcohol is attached to the single bonded oxygen of the acid. The hydrogen lost from the acid and the -OH from the alcohol combine to form a water molecule.



Exercises Condensation Reactions

Write chemical reactions for the following esterification reactions:

1. Ethanol and ethanoic acid
2. Methanol and butanoic acid
3. 2-Pentanol and ethanoic acid
4. Methanol and 2 hydroxybenzoic acid
5. Ethanoic acid and 2-hydroxybenzoic acid



Solutions to exercises

